# Measurements of Volumetric Specific Heat of Thin Films by Means of an AC Calorimetric Method[1]

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## ABSTRACT

Based on the measurement system of an ac calorimetric method, which has been widely applied to measure the thermal diffusivity of thin-film materials, the theory for measuring volumetric specific heat of thin films with an unsteady method is developed in this paper. Several potential causes of experimental error are discussed, with corresponding measures to weaken them. The extensive analysis shows that carrying out the measurement at low heat source frequency, keeping the temperature amplitude of the measured sample equal to that of the referential sample, and limiting the thickness of the samples are necessary for minimizing the systematic error caused by heat loss. The feasibility of this method is testified by measuring the volumetric specific heat of a stainless steel thin film, with a copper film acting as the referential sample.

KEY WORDS: ac calorimetric method; measurement; thin film; volumetric specific heat

## 1. INSTRUCTION

An ac calorimetric method is used extensively to measure the thermal diffusivity of a thin film sample in the direction parallel to the plane surface [1]. In order to calculate the thermal conductivity, the volumetric specific heat of the film is needed, which is the multiplication of density and specific heat. There are many ways to measure specific heat of the materials, such as the calorimeter•the laser pulse method and differential scanning calorimeter[2]. It was also mentioned that the ac calorimetric method is able to measure the specific heat [3]. But in practice, by the principle provided in [3], the measurements to determine the specific heat were not successful. In this paper, the theory for measuring volumetric specific heat of thin films by ac calorimetric method is developed and the preliminary tests showed its feasibility.

## 2. BASIC THEORY

The scheme of measuring volumetric specific heat of a thin film by ac calorimetric method is shown in Fig. 1.

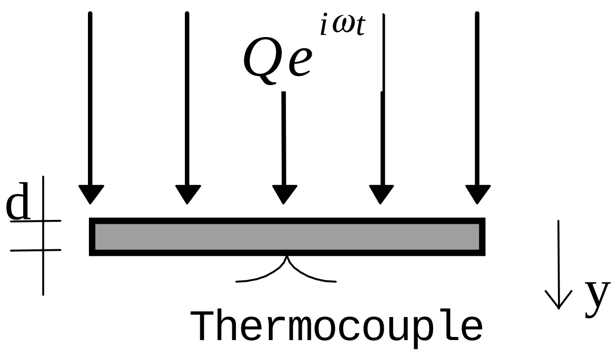


Fig. 1. Scheme of measuring volumetric specific heat of a thin film by ac calorimetric method

A modulated uniform light beam is supplied perpendicularly to the surface of the plate-like thin-film sample. The light energy absorbed by the surface of the sample converts into a uniform heat flux $Qe^{i\omega t}$, which produces a temperature variation on the sample. A fine thermocouple is attached to a point of the sample surface to measure the ac temperature amplitude $|T(t)|$. Under the following hypothesizes:

a. The thermophysical properties of the sample are uniform at different points;

b. The thickness of the sample is small enough.

the thermal balance equation of the sample is:

$$cd\frac{dT}{dt} = -hT + Qe^{i\omega t} \tag{1}$$

When $t \to \infty$, the temperature solution is:

$$T(t) = \frac{Q}{h + i\omega cd}e^{i\omega t} \tag{2}$$

And the temperature amplitude is a constant, which is:

$$A = |T(t)| = \frac{Q}{\sqrt{h^2 + (\omega cd)^2}} \tag{3}$$

The ac calorimetric method used to measure the volumetric specific heat of thin films is a kind of comparative methods. So a referential sample is needed in the measurement. If we have measured the referential sample previously, and got a temperature amplitude:

$$A_{ref} = \frac{Q_{ref}}{\sqrt{h_{ref}{}^2 + (\omega_{ref} c_{ref} d_{ref})^2}} \tag{4}$$

Then the relation between the unknown volumetric specific heat $c$ and the referential volumetric specific heat $c_{ref}$ can be obtained:

$$\frac{c}{c_{ref}} = \frac{\omega_{ref}}{\omega} \cdot \frac{d_{ref}}{d} \cdot \frac{A_{ref}}{A} \cdot \sqrt{\frac{Q^2 - h^2 A^2}{Q_{ref}{}^2 - h_{ref}{}^2 A_{ref}{}^2}} \tag{5}$$

## 3. DISCUSS OF THE SYSTEMATIC ERROR

### 3.1. Systematic Error Caused by Heat Loss

In experiment, if the heat loss of the samples can be ignored, then $h = h_{ref} = 0$. And if the frequency and amplitude of the heat source are kept unchanged, then $Q = Q_{ref}$ and $\omega = \omega_{ref}$. From equation (5), we can get:

$$\frac{c}{c_{ref}} = \frac{d_{ref}}{d} \cdot \frac{A_{ref}}{A} \tag{6}$$

The volumetric specific heat $c$ of the measured sample can be determined easily by equation (6) when neglecting heat loss. However, in practical test, it's impossible to avoid heat loss of the samples, and the exact value of the effective heat transfer coefficients $h$ and $h_{ref}$ are very difficult to calculate. So detailed investigation of the heat loss effect in measuring volumetric specific heat of thin films is required.

Equation (5) can be rewritten as:

$$\frac{c}{c_{ref}} = R \cdot \frac{\omega_{ref}}{\omega} \cdot \frac{d_{ref}}{d} \cdot \frac{A_{ref}}{A} \tag{7}$$

where:

$$R = \sqrt{\frac{Q^2 - h^2 A^2}{Q_{ref}{}^2 - h_{ref}{}^2 A_{ref}{}^2}} \tag{8}$$

It's obvious that all of the uncertain factors in measurement are included in the coefficient $R$, because the heat source frequency $\omega$ and $\omega_{ref}$, the sample thickness

$d$ and $d_{ref}$, and the temperature amplitude $A$ and $A_{ref}$ can be measured directly by the apparatus in experiment. The heat loss of sample is a major factor in affecting the coefficient $R$, which is caused by heat radiation of the sample surface, heat convection of the air, and heat conduction through the thermocouple threads.

3.1.1. Heat radiation of the sample surface

Supposing the sample being a gray body, we can get the heat radiation flux:

$$q = \sigma(\varepsilon_1 + \varepsilon_2)(T^4 - T_0^{\ 4}) \tag{9}$$

where $\sigma = 5.67 \times 10^{-8}$ W/(m$^2$.K$^4$) is Boltzmann's constant, $T_0$ is environment temperature, $\varepsilon_1$ is radiation emissivity of the irradiated surface, and $\varepsilon_2$ is radiation emissivity of the other surface of the sample. When temperature difference $T$ - $T_0$ is small enough, equation (9) can be simplified as:

$$q = 4\sigma(\varepsilon_1 + \varepsilon_2)T_0^{\ 3} \cdot (T - T_0) \tag{10}$$

The effective radiation heat loss coefficient is:

$$h_r = 4\sigma(\varepsilon_1 + \varepsilon_2)T_0^{\ 3} \tag{11}$$

When the environment temperature $T_0 = 300$ K and the sample is a black body, the maximal estimated radiation heat loss coefficient $h_{r,\max} \approx 12$ W/(m$^2$.K).

3.1.2. Heat conduction through the thermocouple threads

For one thermocouple thread, the heat conduction equation is:

$$\begin{cases} \dfrac{\partial T}{\partial t} = \alpha \dfrac{\partial^2 T}{\partial x^2} - h_e T \\ T\big|_{x=0} = Ae^{i(\omega t + \varphi)}, \quad T\big|_{x\to\infty} = 0 \end{cases} \tag{12}$$

where $h_e = \dfrac{8\varepsilon\sigma T_0^{\ 3}}{cr}$, $\varepsilon$ is the radiation emissivity of the thread surface, $r$ is the radius of the thread, and $\alpha$ is the thermal diffusivity. The solution of the equation is:

$$T = e^{-\sqrt{\frac{i\omega + h_e}{\alpha}}x} \cdot Ae^{i(\omega t + \varphi)} \tag{13}$$

The heat flux at the root of the thread is:

$$q = -\lambda \frac{\partial T}{\partial x}\bigg|_{x=0} = \lambda \sqrt{\frac{i\omega + h_e}{\alpha}} \cdot Ae^{i(\omega t + \varphi)} \tag{14}$$

If the thermocouple is attached on the sample by the silver paste, and the radius of the paste is $r_0$, as shown in Fig. 2, then the effective heat transfer coefficient in the silver paste region is:

$$h_t = 4\left(\frac{r}{r_0}\right)^2 \frac{\lambda}{\sqrt{\alpha}}\left(\omega^2 + h_e{}^2\right)^{0.25} e^{i0.5arctg\frac{\omega}{h_e}} \tag{15}$$

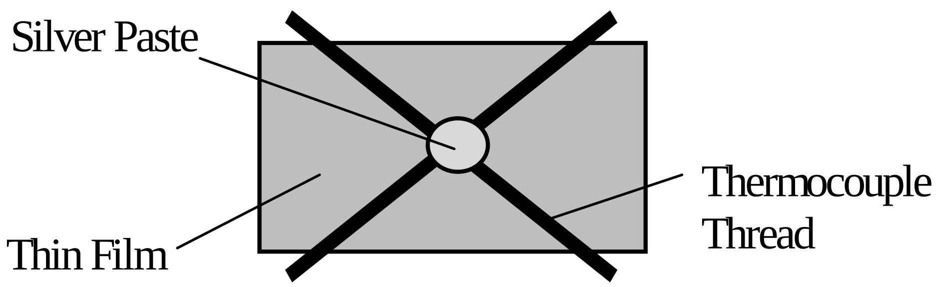


Fig. 2. Connection of the thermocouple and the sample

With a K-typed thermocouple, and $\varepsilon = 1 \bullet T_0 = 300\,\mathrm{K} \bullet r = 12.5 \times 10^{-6}\,\mathrm{m} \bullet r_0 = 0.7 \times 10^{-3}\,\mathrm{m}$, we get:

$$h_t \approx 9.8\left(\omega^2 + 0.0625\right)^{0.25} \cdot e^{i0.5arctg(4\omega)} \tag{16}$$

The above equation shows that measuring at low frequency will decrease the effect of heat conduction through thermocouple threads. When the frequency $\omega$ is

1.0 Hz, the real part of the effective heat transfer coefficient caused by heat conduction through the thermocouple threads is about 25 W/(m$^2$.K), which is comparable to the surface radiation heat loss coefficient $h_r$. Since the flux amplitude of the heat source is about 10$^3$W/(m$^2$), the heat loss effect caused by heat radiation and conduction can be neglected in test. But when the radius of the silver paste decreases or the radius of the thermocouple threads increases, the regional heat transfer coefficient $|h_t|$ will increase rapidly. It's important that the radius of the silver paste is not too small during measuring films with low thermal diffusivity.

The analysis shows that under room temperature and in vacuum environment, the heat loss effect can be neglected in measurement, especially when measuring at low frequency. The effect of the heat loss can not be neglected under the following three circumstances:

a. Measurement is not carried out in vacuum environment. The convection coefficient will be large;
b. Measurement is carried out at high temperature. When $T_0 = 800\,\mathrm{K}$, the maximal estimated radiation heat loss coefficient $h_{r,\max} \approx 232$ W/(m$^2$.K);
c. Measurement is carried out at high frequency. The heat conduction flux through thermocouple thread is large, and the temperature field near the silver paste region is not uniform.

By equation (8), after blackening both sides of the measured sample and the referential sample to insure $Q = Q_{ref}$ and $h = h_{ref}$, and adjusting the heating frequency $\omega$ and $\omega_{ref}$ to make $A \approx A_{ref}$, the coefficient $R$ will equal to 1. Then from equation (7), we get:

$$\frac{c}{c_{ref}} = \frac{\omega_{ref}}{\omega} \cdot \frac{d_{ref}}{d} \cdot \frac{A_{ref}}{A} \tag{17}$$

### 3.2. Systematic Error Caused by Sample Thickness

#### 3.2.1. Lower limit of the sample thickness

When heat loss of the sample is neglected, $R = Q/Q_{ref} = \gamma/\gamma_{ref}$, where $\gamma$ and $\gamma_{ref}$ are light absorptivity of the measured sample and the referential sample. In order to insure $R = 1$, all sides of the samples must be blackened. Since the thickness of the black coating is about 0.1μm, the thickness of the samples must be large enough compared to that of the coating. Usually the thickness of the samples should be greater than 50μm.

Another factor that limits the thickness of the samples is the silver paste. The thickness of the silver paste should be small enough to minimize the possibility that the specific heat of silver paste affects the result of measurement.

#### 3.2.2. Upper limit of the sample thickness

There is an upper limit of the sample thickness, which insures the temperature field on the sample to be uniform. When $t \to \infty$, the heat conduction equation on the sample in Fig.1 is:

$$\begin{cases} \dfrac{\partial T}{\partial t} = \alpha \dfrac{\partial^2 T}{\partial y^2} \\ -\lambda \dfrac{\partial T}{\partial y}\Big|_{y=0} = Qe^{i\omega t} \\ -\lambda \dfrac{\partial T}{\partial y}\Big|_{y=d} = 0 \end{cases} \tag{18}$$

The temperature solution is:

$$T = -\frac{1}{\lambda} \cdot \frac{e^{-2md} \cdot e^{mx} + e^{-mx}}{m\left(e^{-2md} - 1\right)} \cdot Qe^{i\omega t} \tag{19}$$

where $m = \frac{\sqrt{2}}{2}(1+i)k$, and $k = \sqrt{\frac{\omega}{2\alpha}}$ is the reciprocal of the thermal diffusion length.

If the amplitude of the temperature is $A_0$ at $y = 0$, and the amplitude is $A_d$ at $y = d$, by equation (19) we get:

$$\frac{A_d}{A_0} = \frac{2}{\sqrt{\left(e^{\eta} + e^{-\eta}\right)^2 \cos^2 \eta + \left(e^{\eta} - e^{-\eta}\right)^2 \sin^2 \eta}} \tag{20}$$

where $\eta = \frac{\sqrt{2}}{2} kd$.

The calculated curve of equation (20) is shown in Fig.3.

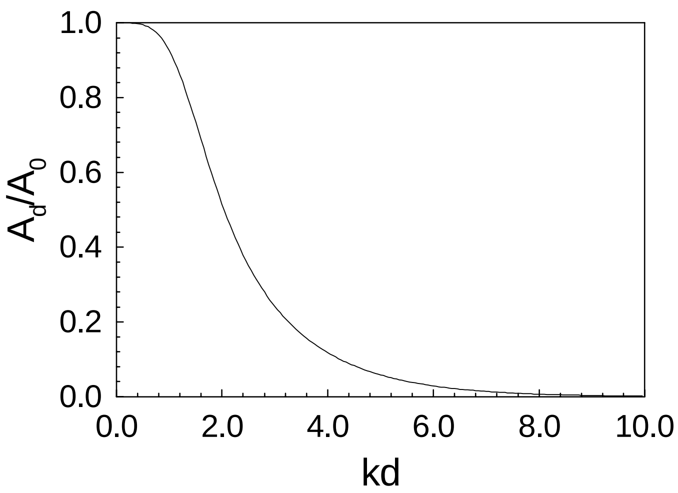


Fig. 3. Decrease of temperature amplitude vs. increase of sample thickness

When $kd < 0.5$, the maximal amplitude decrease in the direction normal to the sample surface is: $\frac{A_0 - A_d}{A_0} < 0.5\%$. When $kd < 0.9$, the decrease of amplitude is: $\frac{A_0 - A_d}{A_0} < 5\%$. So, the thickness of the sample should satisfy the following criteria:

$$d < \sqrt{\frac{\alpha}{2\omega}} \tag{21}$$

## 4. MEASUREMENT SYSTEM

The scheme of the measurement system is shown in Fig.4.

Figure 5 shows the installation of the thin-film sample. The thermocouple is adhered to the sample by silver paste. The maximal dimension of the sample is less than 5mm. And the sample is hung on the specimen mounting by the thermocouple threads. The measurement is carried out in vacuum environment in order to eliminate the convection heat loss.

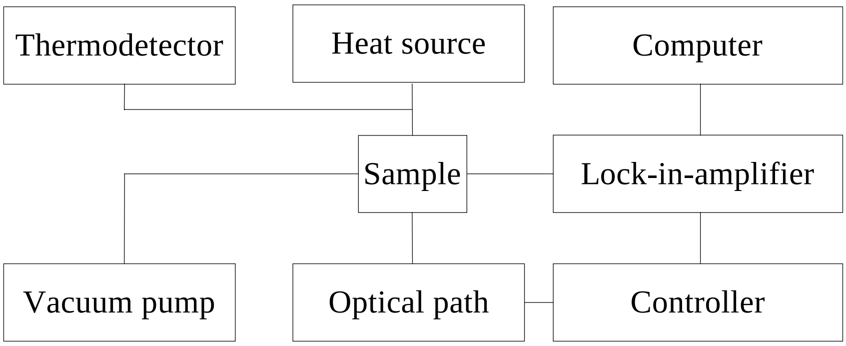


Fig. 4. Scheme of the measurement system

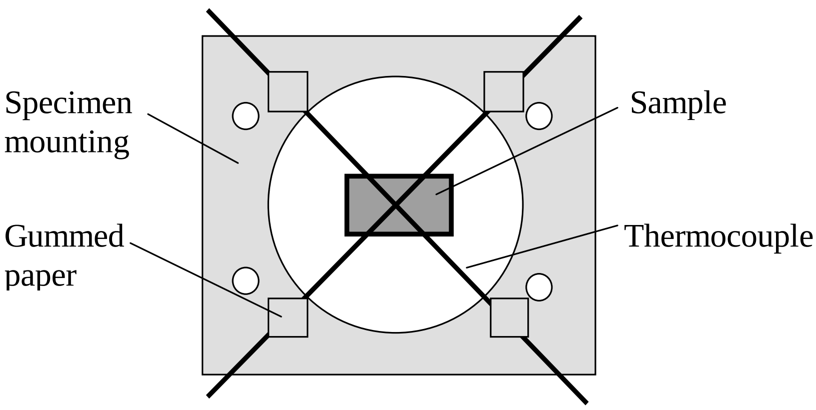


Fig. 5 Installation of the thin-film sample in measurement

In the preliminary test, a copper film with the thickness of 100μm is used as the referential sample. The measured sample is a piece of stainless steel film, with the thickness of 200μm. The results under room temperature are shown in Fig.6-8.

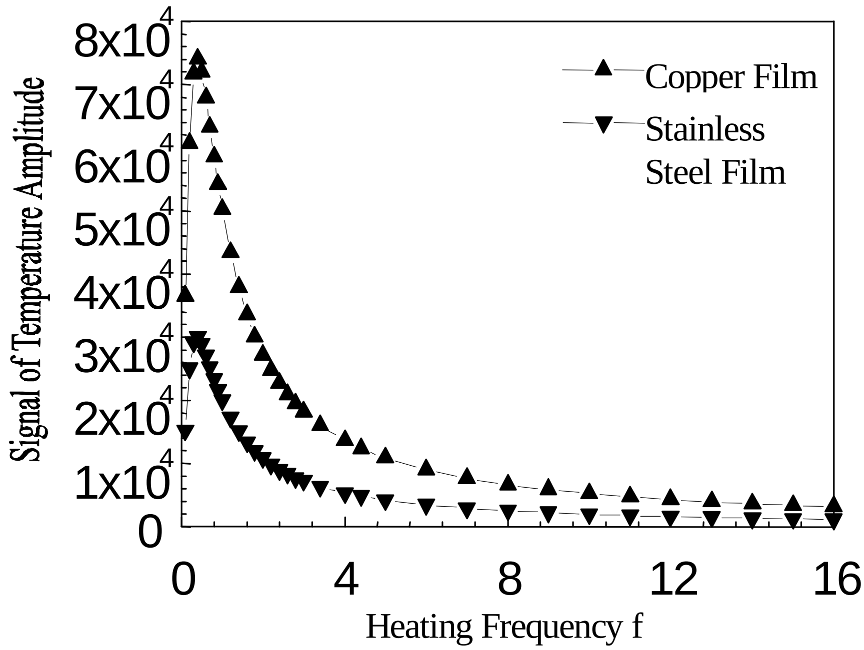


Fig. 6. Signal of temperature amplitude output vs. heating frequency f

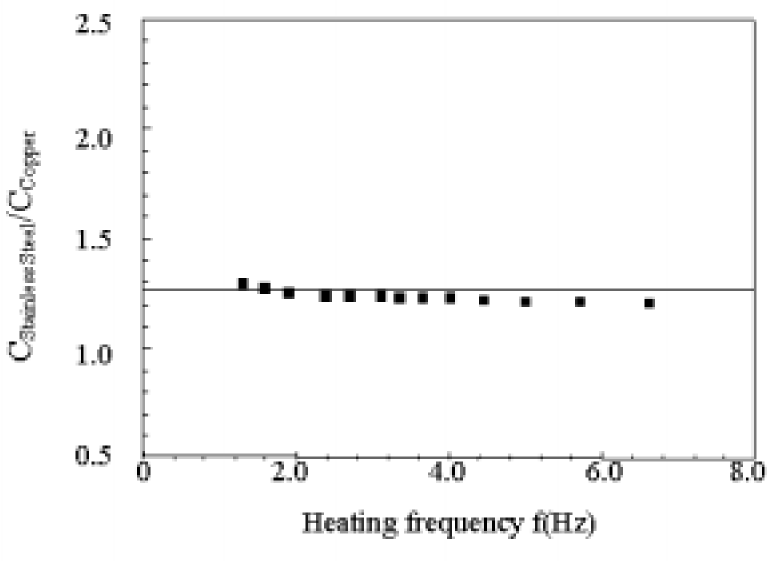


Fig. 7. Measured values while keeping equal temperature amplitudes on the samples

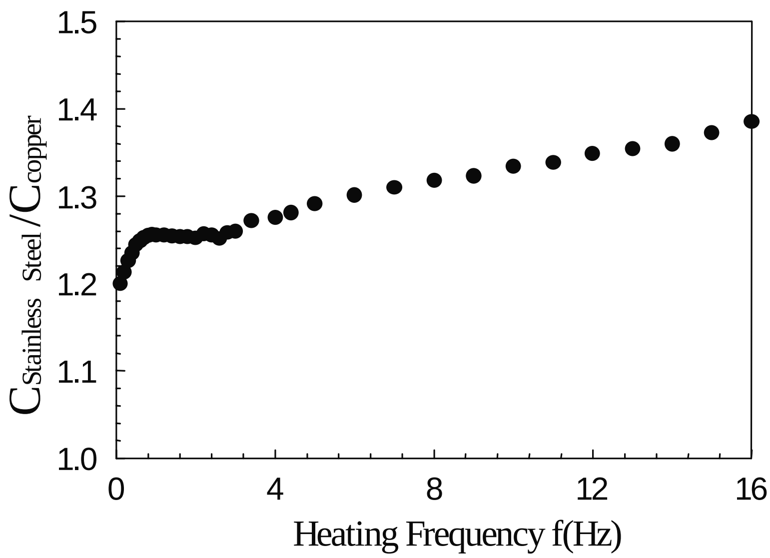


Fig. 8. Measured values while keeping equal heating frequency on the samples

— Referential data[1]

The ratio $c_{stainlesssteel} / c_{copper}$ tends to be a constant when the heating frequency is greater than 2 Hz. The result testifies the feasibility of the theory of measurement. Since the magnification of the lock-in-amplifier changed in the frequency region less than 2 Hz, the measured value in this region deviated from the actual value of the sample.

**4. CONCLUSION**

The theory and method of measuring volumetric specific heat of thin films are explained in the paper. Some causes of systematic error, such as heat loss of the samples and the sample thickness, are discussed in detail. Base on the analysis, several valuable criteria that should be considered in measurement are obtained. They include the following key points:

a. Measuring at low frequency;

b. Keeping the temperature amplitudes of the measured sample equal to that of the referential sample by adjusting the frequency of heat source;

c. Ensuring the thickness of the sample less than half of the thermal diffusion length;

d. Decreasing the thickness difference between the measured sample and the referential sample;

e. Blackening all sides of the measured sample and the referential sample to ensure that the surfaces have the same light absorptivity;

f. Unifying the temperature field near the thermocouple by using very thin silver paste with large radius when measuring the films with low thermal diffusivity.

The above theory and measurement technique are testified in the preliminary test, in which the referential sample is a copper film and the measured sample is a stainless steel film.

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